PB-217 045

A COMPARATIVE STUDY OF OXYGEN CONSUMED METHODS

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5 September 1950

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A COMPARATIVE STUDY OF OXYGEN CONSUMED METHODS*

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During the past few years several methods have been proposed for the determination of oxygen consumed values of organic wastes. This is because the shortcomings of the American Public Health Association's permanganate method are well known and there is a definite need for a better oxygen consumed method for stream sanitation and industrial waste studies. In order to evaluate the various proposed methods a comparative study was made by this laboratory. In addition to the Permanganate or Standard Method (1) the other methods studied include the dichromate method proposed by Ingols and Murray (2), the dichromate method proposed by Madison (3), the iodic acid method of Dzyadzio (4), as modified by Johnson, Tsuchiya and Halvorson (5), and the dichromate method proposed by Moore, Ruchhoft and Kroner (6) of this Center. Shortly after the study was started the use of silver sulfate as a catalyst for dichromate oxygen consumed procedures as proposed by Muers (7) was added to the modifications used.

Experimental

In the present study, four organic compounds which are typical of those ~~that~~ might be found in sewage and industrial wastes were used. In addition, a study of four industrial wastes was made. Although other industrial wastes were available, only those were selected that would be stable over the period necessary to carry out the comparison.

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*Presented at the 118th National Meeting of the American Chemical Society, Chicago, Illinois, September 3-8, 1950

Ten replicates were run at a time by each of the methods studied except the one using iodic acid as the oxidizing agent. Only five replicates could be conveniently run at the same time when the iodic acid method was used. In each case an equal number of blanks were run except when the check results on blanks assured that a smaller number would be sufficient. Tests were run by each method on various sample volumes within the range permitted by the amount of available oxidizing agent. Over one-half the samples were so tested in order to check the effect of sample size.

The effect of different reflux times on the oxygen consumed values was evaluated on the Moore method to determine whether the specified two hour period could be shortened.

The iodic acid method was checked to determine the effect of the volume of the reflux mixture (with a constant sample volume) on oxygen consumed results by adding various amounts of distilled water to the reaction mixture before refluxing.

Results

Table I presents the statistical data obtained on all of the samples. On the first two samples 100 replicates were run by each method. Because of accidental factors which gave results not representative of the method or sample, a few of the determinations were discarded and statistical data were calculated on the basis of the remaining replicates.

Sample No. 1 indicated an oxygen consumed of nearly the same magnitude for both the Moore and Ingols' procedure. However, the range of results of Ingols' and particularly the Madison method was excessive. Although the standard deviation of the permanganate method places it second on this sample, the order of magnitude of its coefficient of variation indicates that it is inferior to all the methods except that of Madison.

On Sample No. 2 the iodic acid method gave the highest percentage recovery although in reproducibility it was inferior to both Moore's and Ingols' methods. As with the first sample the order of magnitude of the coefficients of variation place the permanganate method fourth, it being only slightly better than Madison's procedure.

On Sample No. 3 the iodate methid again gave the highest oxygen consumed of all except the Moore procedure using silver sulfate as a catalyst. The reproducibility of the iodate procedure was very poor, poorer reproducibility being shown only by the Madison method. The coefficients of variation on this sample were in the same order as with the previous two samples.

The data were subjected to an analysis of variance to ascertain whether the number of samples could be reduced without losing statistical reliability. Both the Bartlett test and the Fisher Variance Ratio (8) were applied to the data to determine whether individual groups of replicates were reasonably representative of a larger number of replicates. The Madison and permanganate procedures were found to show groups of replicates which could not be considered

as part of the normal variation of the replicates as represented by all determinations made. The results obtained by the iodate procedure fell in a doubtful zone on the basis of the Bartlett and Fisher tests. The Ingols and the Moore procedures were found to show either satisfactory performance or significant statistical variation only on the basis of a variation of no practical importance from the standpoint of the application and use of the analysis. For example, a difference in variance from one to ten will give the same order of results by these tests as another group with variance differing by 1,000 to 10,000. When the variance is of very low order compared to the value of the mean, the variance ratio test is of little value in the evaluation of reproducibility of analytical technique.

The data on confidence limits included in Tables I and II are 95 per cent confidence limits which means that either the single determination or the mean as indicated in the table will be within the limits stated 19 out of 20 times.

On the basis of the data assembled on the first three samples, the Madison and permanganate procedures were dropped and another procedure, consisting of the basic Moore method modified by the addition of silver sulfate in the reflux mixture, was added to the list of methods given further study.

As a result of this work, it was judged feasible to decrease the number of replicates for each method to 20 for the remainder of the study with each group of five or ten replicates obtained on different days.

This made it possible to use industrial wastes which were not stable enough to be used over the long period of time required for the greater number of determinations used in the first three samples.

With Sample No. 4, (Table I), the iodate method not only resulted in very poor reproducibility but also in a lower oxygen consumed value as well. The use of the Moore procedure, modified by addition of the silver sulfate resulted, on this waste, in a reduction of oxygen consumed of 40 to 60 per cent. Definite signs of incompatibility between catalyst and sample were noted as soon as refluxing began.

The iodate method oxidized Sample No. 5 from five to 20 per cent whereas the dichromate methods resulted in uniform high oxidations. With two different standard solutions of iodate, the results on Sample No. 5 ranged from 45 to 133 p.p.m. oxygen consumed. A similar situation was evident in a filtrate from a waste containing naphthol sulfonic acid. On the latter material, the iodate method would not give a consistent oxygen consumed value, while the dichromate methods yielded consistent results on the order of 60,000 p.p.m. Since this sample changed from day to day, it could not be included in this study. After the work on these samples, the iodate procedure was dropped from the study.

A distillery waste, Sample No. 6, was high in organic acids such as acetic, propionic and lactic. Hence, the silver sulfate method responded very well both from the standpoint of recovery and reproducibility. The results obtained with Samples Nos. 7 and 8 indicate no definite superiority for any of the dichromate reflux methods used.

The minimum safe number of replicates [9], required to produce a mean (95 per cent confidence limits) within two per cent of the mean of a large number of determinations on the same sample, is given in Table III. The data presented in Table III were calculated according to the following formula:

$$\frac{s}{\sqrt{n}} \times t_n \leq 0.02\,\bar{x}$$

where s = standard deviation on a large number of individual determinations

n = indicated minimum number of replicates

t_n = Fisher's "t" value for "n" replicates at 95 per cent C. L.

$\bar{x}$ = mean of a large number of individual determinations.

The allowance of two per cent of the mean is an arbitrary figure used on all samples, the remainder of the values are taken from tables or calculated from the data obtained on the samples. This value is quite exacting in its evaluation of a method and rapidly increases in severity when the degrees of freedom for "n" approach one as an inspection of a table of "t" values will show. For this reason a minimum safe number of replicates of less than three would be unusual.

The results as given in Table III indicate by the use of this parameter that with the exception of the last two samples, both the

unmodified Moore method and the catalyst modified method are statistically superior to any of the methods tested. It was partially on the basis of these results that the iodate method was eliminated from further consideration.

Factors Affecting Oxygen Consumed Results

The time required for determination of the number of replicates and blanks indicated is given in Table IV. Both the total elapsed time and the manipulation time are given. The reflux time required no personal attention except in the iodate method where bath temperatures must be held within $\pm$ 5° of 190°C. In Madison's method closer attention is required than in any of the others as the determination of the endpoint in the digestion cycle is vague, and the heating rate must be carefully controlled.

Other factors such as recognition of titration endpoints, size of sample used, rate of heating, etc., are important in the selection of the most efficacious method. The following discussion is designed to bring out these points that would not be noticeable except to those who used the methods repeatedly.

While the permanganate method requires less time than any of the other methods it is very difficult to obtain uniformity in results. Heating in a water bath is subject to variation especially when running large number of replicates. In some cases a given sample may boil more rapidly than others and concentrate the mixture with resulting difference in the oxygen consumed value. The effect of agitation is also very noticeable on the oxygen consumed, as the reaction mixture

tends to precipitate manganese dioxide to a certain extent and if not agitated frequently variable results are obtained. In some cases, this precipitate is difficult to redissolve before titrating the sample. The titration endpoint is definite but since the permanganate color fades slowly the titration has to be conducted slowly and carefully to obtain permanent endpoints. Different analysts following the same methods of manipulation produce results which vary appreciably. The effect of sample size is significant, hence the use of as close to 50 per cent of the oxidizing agent as possible is desirable in order to avoid variable results.

In Madison's method the amount of oxidizing agent available is small which limits the size of the sample that can be used. This tends toward large errors when strong industrial wastes are tested. The major objections to this method are in the close attention required over a prolonged period and the difficulty in detecting the digestion endpoint. The digestion period is terminated when the concentrated sulfuric and phosphoric acid mixture has fumed for exactly four minutes. It is imperative that the first traces of fuming be detected, otherwise if fumed too long the oxidizing reagent is decomposed. Blank determinations give poor agreement as a result of the difficulty in stopping the digestion at the right time. The titration using sodium diphenylamine sulfonate as an indicator requires a lapse of time between additions of the ferrous ammonium sulfate before there is any noticeable change in the color of the indicator. There is no chance to judge when the endpoint is being approached so that back titration

is frequently necessary. Use of different sample volumes gives good reproducibility, providing not more than 50 per cent of the oxidizing agent is used.

The iodate method requires more equipment, time and manipulation than any of the other methods tried. The use of the phosphoric acid bath to control reflux temperature is a definite hazard. The substitution of a bath wax reduces this hazard to a certain extent, although no improvement is affected in manipulation or time involved. The large volume of solution required for the steam distillation makes later cooling a problem, but if a smaller volume is used in this stage, recovery is low due to incomplete separation of the iodine formed during the reflux period. The titration of a 500 ml. aliquot of sample is cumbersome to carry out. Poor checks were obtained on blanks throughout the study. The agreement in oxygen consumed values for different sample volumes was good providing total sample volume did not exceed 40 ml. Above this volume, there was a definite drop in the oxygen consumed even though only distilled water was added to the reaction mixture. This is due to the fact that such mixtures boiled vigorously below the 190°C. temperature specified in the method. The method is not applicable to as large a variety of samples as is the case in the dichromate oxidations, however, if the iodic acid is effective on a given sample its percentage recovery may be higher than those by other methods.

Ingols' method has been shown to give fair results with a wide variety of samples and requires little time and manipulation. However, reproducibility is poor, especially on strong wastes where the size of the sample that can be used is small. The reagent mixture is quite unstable and must be freshly prepared about every two weeks. The titration of iodine with thiosulfate to the starch iodide endpoint in the presence of chromic salts is particularly poor as the endpoint is masked by the confusing colors. Different analysts can obtain appreciable differences due to this factor. To treat a blank differently than the sample itself is generally considered poor technique. However, in the case of Ingols' method if the blank is refluxed more or less of the dichromate is decomposed, the amount of such decomposition depending upon several factors. For this reason, the cold blank was used as recommended in the original procedure and the results do not appear to be affected to any appreciable extent. The use of different sample volumes has little effect on the oxygen consumed values.

The Moore method is intermediate as far as time required and apparatus involved. The endpoint is very sharp and after a little experience an analyst knows approximately how close to the endpoint he may be as the color changes from a yellow through various shades of green to blue, then sharply to a red-blue at the endpoint. Very little effect on the results obtained is noted regardless of sample size, in fact, close checks have been obtained when the back titration was only two to three drops. The ferrous ammonium sulfate requires

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standardization daily since the acid concentration is kept purposely low (20 ml. concentrated H_2SO_4 per liter) and its normality gradually decreases. However, the standard dichromate solution is stable over long periods of time. The endpoint is sharp when the concentration of sulfuric acid in the titrating mixture does not exceed 30 per cent, hence the reaction mixture must be diluted before titration and the acid content of the standard ferrous ammonium sulfate must be controlled in order to obtain a satisfactory endpoint. Little difference was observed in results obtained by different analysts. Sample volume is not critical although results on purified effluents may not be too reliable due to the small consumption of the oxidant with the consequent high back titration. Refluxed blanks check very well and normally do not show a depletion of more than 0.10 ml.

The two hour digestion period was subject to some question, hence digestion periods of one-half, one and two hours were tried on several samples. On most samples, one-half or one hour would be sufficient, however, the one-half hour reflux time on Sample No. 3 in Table I resulted in an 18 per cent lower, and the one hour digestion an 11 per cent lower oxygen consumed than results obtained on the two hour reflux period. Glycocoll exhibited similar behavior. Therefore, it is well to check different reflux times on a given sample before attempting to shorten the two-hour reflux period. If no significant difference in the results is obtained, the shorter time may very easily be adopted.

Effect of Silver Sulfate as a Catalyst

In Table V the effect of one gram of silver sulfate in conjunction with the regular Moore method was checked on 17 different compounds in order to evaluate its applicability. It will be noted that acetic acid is virtually unaffected by acid dichromate alone while with the silver sulfate, oxidation is better than 95 per cent of theoretical. Other compounds tried resulted in varying degrees of improvement on oxygen consumed values but substantial improvement was obtained in 14 of the 17 compounds used. Particularly good results are obtained when using the catalyst on short chain carbon acids. Certain compounds tend to precipitate the silver and either nullify its effects or actually result in a lower oxygen consumed value than the method without catalyst. This is generally true when the sample has a high concentration of chlorides. The precipitated silver also causes some difficulty in determining the endpoint due to turbidity effects. Sample No. 3 in Table I was one of those which decreased the oxygen consumed value upon addition of silver sulfate.

Silver sulfate as a catalyst is recommended as a complement to the regular procedure rather than a substitute as there are apparently many wastes which show incompatibility. If work is to be done on a given type of waste, it would be beneficial to use both the regular and the catalyzed methods and select the one giving the better results. Neither the Ingols' nor the iodate method is applicable with the silver sulfate due to the reaction with the added iodide before titration.

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Conclusions

1. Application of statistical procedures to the data leads to the conclusion that Moore's method is preferable to the other methods tested for the determination of the oxygen consumed value.
2. This conclusion is also reached from the standpoint of ease of manipulation and the applicability to a large variety of samples and the time required.
3. The use of silver sulfate as a catalyst for dichromate oxygen consumed reactions appreciably extends the useful range of the procedure. On most compounds or mixtures and especially with straight chain acids an increase in the theoretical oxidation is noted. With a few compounds, or in the presence of high chloride concentration, the use of the catalyst is precluded, making it necessary to check both modifications. Certain materials such as benzene, toluene and pyridine are not oxidized by either procedure.

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TABLE I

Statistical Comparison of Oxygen Consumed Methods

Sample Number	Compound or Waste and Method Used	No. of Determinations[1]	Mean	Range	Standard Deviation	Confidence Limits[2]	Coefficient of Variation	Per cent of Theoretical
1	Organic Dye Waste							
	Iodate	99	960	223	39.4	110	.041	-
	Ingols	96	1153	591	73.6	166	.064	-
	Madison	99	690	1184	211	466	.306	-
	Permanganate[3]	98	463	169	33.3	75	.072	-
	Moore	100	1183	113	15.9	36	.013	-
2	Ortho-cresol							
	Iodate	99	575	79	14.0	39	.024	91.4
	Ingols	98	543	80	12.9	29.1	.024	86.3
	Madison	99	459	174	30.5	68.9	.066	72.9
	Permanganate[3]	99	443	100	22.8	51.5	.051	70.5
	Moore	100	530	31	5.1	11.6	.001	84.2
3	Oil Refinery Caustic Waste							
	Iodate	49	50900	8182	2274	6322	.045	-
	Ingols	50	46000	3680	874	1976	.019	-
	Madison	50	32200	19360	2838	6413	.088	-
	Permanganate[3]	50	29100	10040	1232	2784	.046	-
	Moore	50	48400	1843	347	783	.007	-
	Moore-Ag_2SO_4	29	57500	3230	742	1676	.013	-

(Continued)

TABLE I (Continued)

Sample Number	Compound or Waste and Method Used	No. of Determinations (1)	Mean	Range	Standard Deviation	Confidence Limits (2)	Coefficient of Variation	Per cent of Theoretical
4	Textile Dye Waste							
	Iodate	20	27477	6674	1634	4543	.060	--
	Ingols	20	35209	2313	569	1285	.016	--
	Moore	20	36599	786	204	461	.006	--
	Moore-Ag_2SO_4 (4)	--	--	--	--	--	--	--
5	Glycocoll (5)							
	Iodate	10	--	--	--	--	--	--
	Ingols	20	417	76	18.3	41.4	.044	65.2
	Moore	20	592	19	4.5	10.2	.034	90.8
	Moore-Ag_2SO_4	20	607	20	4.5	10.2	.033	94.8
6	Distillery Waste							
	Ingols	20	356	38	14.8	33.4	.041	--
	Moore	20	344	19	6.0	13.6	.018	--
	Moore-Ag_2SO_4	20	902	24	5.3	11.9	.006	--
7	2-Amino-8-Naphthol-6-Sulfonic Acid (6)							
	Ingols	20	1320	52	13.8	31.1	.010	79.4
	Moore	20	1336	25	6.1	13.9	.005	80.4
	Moore-Ag_2SO_4	20	1356	35	10.3	23.4	.008	81.8
8	Sodium Lauryl Sulfate (7)							
	Ingols	20	1436	62	16.9	38.1	.012	71.8
	Moore	20	1527	68	15.3	34.9	.010	76.4
	Moore-Ag_2SO_4	20	1812	106	23.0	52.0	.013	90.7

(Continued)

TABLE I (Continued)

(1) Ten replicates were run on all methods except the Iodate where five replicates were run.

(2) Ninety-five per cent Confid- ce Limits of a single determination.

(3) American Public Health Association Standard Method.

(4) Silver sulfate could not be used as a catalyst on this waste, resulted in 40 to 60 per cent lower value than regular procedure.

(5) Replicate determinations varied from 45-133 p.p.m. and less than 10 per cent of theory was obtained.

(6) Technical grade.

(7) Technical grade probably a mixture of lauryl sulfates.

TABLE II

Ninety-five Per cent Confidence Limits of the Mean on the Number of Replicates Indicated in Table I

Sample	95 Per cent Confidence Limits Mean					
	Ingols	Iodate	Madison's	Permanganate	Moore	Moore-Ag_2SO_4
Organic Dye Waste	6.2	5.5	10.4	4.1	2.8	-
Ortho-cresol	2.9	3.3	4.0	3.4	1.6	-
Oil Refinery Caustic Waste	282	694	927	394	111	311
Textile Dye Waste	287	1016	-	-	103	-
Glycocoll	9.2	-	-	-	2.3	2.3
Distillery Waste	7.5	-	-	-	3.1	2.6
2-Amino-8-Naphthol-6-Sulfonic Acid	7.0	-	-	-	3.1	5.2
Sodium Lauryl Sulfate	8.5	-	-	-	7.8	11.6

TABLE III

Minimum Safe Number of Replicates for Each Method with Each Sample

Sample	Ingols	Iodate	Madison	Permanganate	Moore	Moore-Ag_2SO_4
Organic Dye Waste	42	18	100+	52	5	- (1)
Ortho-cresol	8	9	45	28	4	-
Oil Refinery Caustic Waste	6	22	75	22	3	5
Textile Dye Filtrate	6	37	-	-	3	-
Glycocoll	21	- (2)	-	-	3	3
Distillery Waste	19	-	-	-	6	3
2-Amino-8-Naphthol-6-Sulfonic Acid	4	-	-	-	3	3
Sodium Lauryl Sulfate	4	-	-	-	4	5

(1) No results were obtained with silver catalyst on first two samples.

(2) Iodate Method too variable and gave less than 10 per cent theoretical recovery.

TABLE IV

Time Study on Various Oxygen Consumed Methods

	Ingols'	Iodate	Madison's	Permanganate	Moore
Number of Replicates Determined (1)	10	5	10	10	10
Total Hours Elapsed	3.75	7.75	7	3	4.50 (2)
Manipulation Time (Hours)	2.75	7	7	2.50	2.50

(1) In each case an equal number of blanks were run in the time indicated.

(2) Use of silver catalyst involves only the solution of silver sulfate in the concentrated sulfuric acid stock, otherwise time and manipulation is the same as the regular procedure. Used one gram Ag_2SO_4 for each 75 ml. acid.

TABLE V

Effect of Silver Sulfate on Moore Oxygen Consumed Method

Compound[1]	Regular Per Cent			With Ag_2SO_4		
	Mean	Range	Per cent Theory	Mean	Range	Per cent Theory
Acetic Acid	26	38	2.4	104	62	95.1
Alanine	362	25	33.5	870	17	80.6
ε-Amino-n-Caproic Acid	1790	40	97.7	1804	26	98.5
Benzene	240	18	7.8	250	28	8.1
n-Butyric Acid	1306	34	71.8	1748	18	96.1
Chlorbenzene	252	176	25.4	410	95	41.4
Ortho-cresol	2095	54	83.2	2413	43	95.8
Ethanol[2]	619	67	29.7	1672	33	80.1
Furoic Acid	1074	57	83.6	1254	14	97.6
Glutanic Acid	626	78	63.9	980	17	100
Lactic Acid[3]	484	28	45.4	882	13	82.7
Oleic Acid	1805	150	62.4	2246	83	77.7
Pyridine	34	6	1.3	20	17	0.8
Sodium Stearate	2018	124	74.2	2494	36	91.7
Toluene	671	40	21.4	704	89	22.5
Turpentine	1206	706	36.9	1528	839	46.8
Valone	1295	77	78.9	1573	94	95.9

(1) Ten replicates of each compound with and without the silver catalyst were run.
(2) Eighty-seven per cent C_2H_5OH
(3) Impure grade of lactic acid.